

GAS-CHROMATOGRAPHIC MEASUREMENTS OF ATMOSPHERIC CF₂Cl₂, CFCl₃ AND N₂O IN ANTARCTICA

Michio HIROTA, Shigeru CHUBACHI, Yukio MAKINO
and Hisafumi MURAMATSU

*Meteorological Research Institute,
1-1, Nagamine, Yatabe-machi, Tsukuba-gun, Ibaraki 305*

Abstract: Atmospheric CF₂Cl₂, CFCl₃ and N₂O were measured by a gas-chromatographic method. Air samples were obtained by the 23rd and 24th Japanese Antarctic Research Expeditions. Vertical distributions of these gases over Syowa Station were observed on January 24, 1983, and they showed very uniform distributions up to an altitude of 6.4 km. Mean volume mixing ratios and their standard deviations for five samples were 32₁ and 3 ppt for CF₂Cl₂, 18₂ and 6 ppt for CFCl₃, and 29₈ and 2 ppb for N₂O, respectively. Mean values of CF₂Cl₂ and CFCl₃ were lower than those observed over Japan from October 1982 to February 1983 by (4±3)% and (6±7)% respectively. A similar result was also obtained in the latitudinal distribution of CF₂Cl₂ from Japan to Syowa Station (November 1982–January 1983). CF₂Cl₂ and CFCl₃ at Syowa Station showed rather large rates of increase during 1982 (2₈ and 1₈ ppt/year). In the same period, N₂O was quite constant ((29₈±3) ppb) at Syowa Station.

1. Introduction

Atmospheric CF₂Cl₂, CFCl₃ and N₂O are major sources of stratospheric ClO_x and NO_x. It is well known that CF₂Cl₂ and CFCl₃ released by man's activities are being accumulated in the atmosphere, and these gases including N₂O are very stable in the atmosphere except for photodissociations and chemical reactions with O(¹D) in the stratosphere (MOLINA and ROWLAND, 1974). Therefore, the atmospheric distributions and variations of these gases have received intensive investigation since the mid-1970's in order to assess their influence on stratospheric ozone (NATIONAL ACADEMY OF SCIENCES, 1979a, b; WMO, 1980).

We have measured these gases over Japan since 1978 (HIROTA *et al.*, 1984). Measurements of air samples in Antarctica (or in the southern hemisphere) are also indispensable to understanding the global distributions of these gases (RASMUSSEN *et al.*, 1981), because most CF₂Cl₂ and CFCl₃ have been released in the northern hemisphere. In addition, it is considered that the influence of local air pollution is rather small in Antarctica.

Air samples were obtained by the 23rd and 24th Japanese Antarctic Research Expeditions (JARE-23 and -24), and analyzed by a gas-chromatographic method. In this paper, preliminary results of 1) latitudinal distributions from Japan to Syowa Station, 2) vertical distributions over Syowa Station, and 3) time trends at Syowa Station will be reported.

2. Experimental

2.1. Sampling of air

Air samples from Japan to Syowa Station were collected on the bridge of the icebreaker FUJI (~ 14 m above the sea surface). Air samples at Syowa Station were collected 130–170 m northeast from a hut of the Upper Atmosphere Physics Laboratory. Sea surface air and air at Syowa Station were sucked through a copper tube ($3/8''$ or $1/4''$ o.d.) into a stainless-steel cylinder (0.3 l) by an air pump (GAST DOA-101) as shown in Fig. 1.

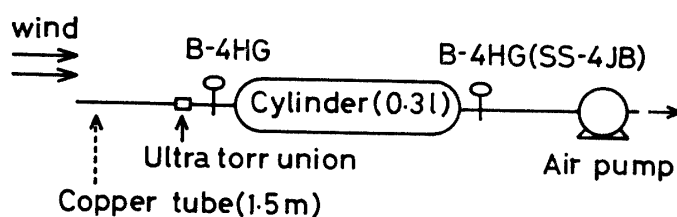


Fig. 1. Air sampling apparatus. Valve; B-4HG or SS-4JB (Nupro), union; Ultra torr union (Cajon), pump; DOA-101 (GAST).

Air samples over Syowa Station up to the altitude of 6.4 km were collected on an aircraft "Pilatus PC-6". On the aircraft, a copper tube was installed in the stay of the wing in order to avoid the exhaust gas from the engine, and air was taken utilizing dynamic pressure.

In 1982 at Syowa Station (JARE-23), the air pump was set before a cylinder, and air was pumped in up to the pressure of 4–5 kg/cm². However, this method was changed to the one mentioned above in order to avoid possible contamination from the air pump diaphragm.

Sampling cylinders were heated to 350°C and evacuated by an oil rotary vacuum pump before shipping. In the sampling cylinder, contents of CF_2Cl_2 , CFCl_3 and N_2O were all constant for several months within the range of experimental uncertainty. However, stabilities of these gases in the cylinder could not be ascertained for more than one year in very cold conditions. Stabilities over a longer period are now being examined.

2.2. Gas-chromatographic analysis

CF_2Cl_2 , CFCl_3 and N_2O in the sample air were analyzed using a Shimadzu Gas Chromatograph GC-6AM equipped with an electron capture detector (ECD-4). The sample air in the cylinder was transferred to a gas sampler (Carle 2021 six-port valve), and then to the gas chromatograph. Gas-chromatographic conditions are summarized in Table 1 (HIROTA *et al.*, 1984). In the calculation of concentrations, peak heights of gas chromatograms were used. Concentrations are all shown by volume mixing ratios, where ppt = 10^{-12} , ppb = 10^{-9} , and ppm = 10^{-6} . Apparent volume mixing ratios of CF_2Cl_2 were dependent on the pressure of sample airs, and corrections were added after measurements.

Table 1. Gas-chromatographic conditions (HIROTA *et al.*, 1984).

Species	CF ₂ Cl ₂	N ₂ O	CFCl ₃
Column	glass column 3 m×3 mm i.d.		
Packing	molecular sieve 5A (30–60 mesh) 20% silicone oil DC-200, chromosorb WAW (60–80 mesh)		
Temp.	90°C	245°C	60°C
Carrier gas	ultra pure N ₂ (99.9995%) passed through a drier tube filled with molecular sieve 5A (1/16" pellets)		
Flow rate	40 ml/min		
Detector	ECD ⁶³ Ni 10 mci		
Pulse	width; 8 μs, height; 40V, freq.; 2.5 kHz		
Temp.	320°C		
Sample size	2 ml		1 ml

2.3. Reference gas

A mixed gas of 20 ppm CF₂Cl₂ and 20 ppm CFCl₃ in nitrogen gas (Nihon Sanso) was used as a primary reference gas for CF₂Cl₂ and CFCl₃. In order to make a reference gas for practical use, 200 μl of this gas was diluted with 10 l ultra pure nitrogen gas (99.9995%), which was passed through a U-shaped glass tube filled with active carbon (30–60 mesh, 0°C), into a *tedlar* bag just before the analysis.

The preparation method of a reference gas for N₂O was changed from the previous method (HIROTA *et al.*, 1984) in order to reduce the dilution factor of the primary reference gas. Air (Hitachi Sanso), which contained about 0.3 ppm N₂O, was used as N₂O reference gas. The volume mixing ratio of N₂O in that air was determined by comparing it with a secondary reference gas, which was made by diluting a primary reference gas (N₂O=970 ppm, Takachiho) with ultra pure N₂. In dynamic dilution of the primary reference gas, a Standard Gas Generator SGGU-72AC3 (Standard Technology) was used.

Uncertainties and detection limits in the measurements are summarized in Table 2 (HIROTA *et al.*, 1984).

Table 2. Errors in the gas-chromatographic analysis for the tropospheric air samples (HIROTA *et al.*, 1984).

Species	CF ₂ Cl ₂	CFCl ₃	N ₂ O
Detection limit	1 ₅ ppt	4 ppt	1 ₀ ppb
Mixing ratio in ref. gas	43 ₄ ppt	41 ₄ ppt	30 ₃ ppb
Error in repeated measurements of a ref. gas	1.9%	0.6%	1.5%
Error in measurements of several ref. gases	2.3%	3.2%	
Error in repeated measurements for samples	±1.0%	±0.9%	±2.0%

3. Results and Discussion

3.1. Latitudinal distribution

Latitudinal distribution from Tokyo to Syowa Station was obtained only for CF_2Cl_2 , and is shown in Fig. 2. Samples were collected at intervals of about 5° . Values of three samples at 26° , 20° and 16°N were larger by 7–70% than the mean north of the equator except for these three values (35_6 ppt). These three samples would have been contaminated with the air on board due to inexperience in operations for the first four samples.

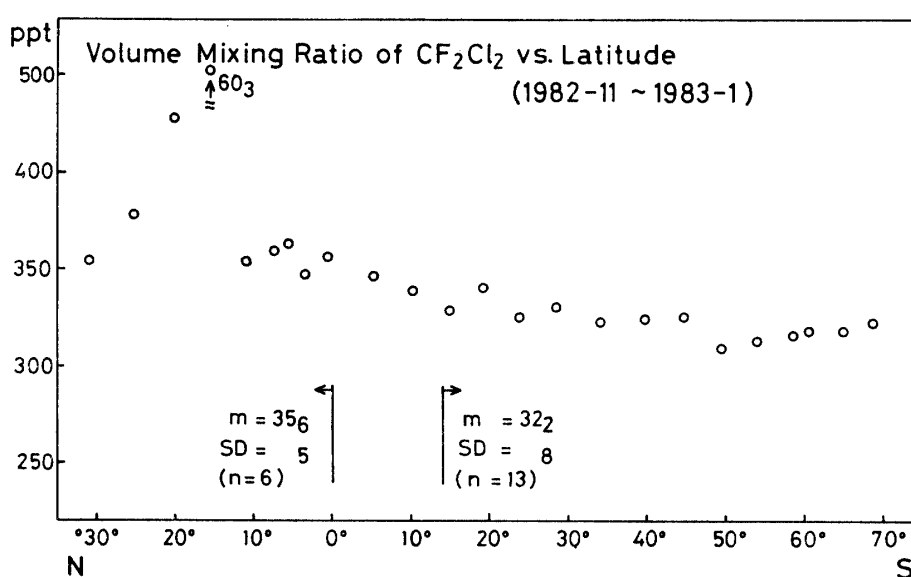


Fig. 2. Latitudinal distribution of CF_2Cl_2 . Three samples between 26° and 16°N were contaminated with the air on board.

Mixing ratios decreased gradually from the equator to 15°S . It is known that the intertropical convergence zone (ITCZ) moves into the summer hemisphere between the Central Pacific Ocean and the Indian Ocean. From cloud images and cloud wind vectors (850 mb) of the Geostationary Meteorological Satellite, ITCZ seemed to exist between the equator and 10°S in agreement with our observations early in December 1982.

The ratio of the mean volume mixing ratio south of 15°S (32_2 ppt) to that north of the equator (35_6 ppt) was 0.90 (0.87–0.94). Assuming a two-box model (northern and southern hemisphere) (CHANG and PENNER, 1978) with an interhemispheric exchange time of 1 year, and CF_2Cl_2 release data of the Chemical Manufacturers Association (CMA, 1983), this ratio (0.90) corresponds to an atmospheric lifetime of a few hundred years (lower limit = 50 years). CF_2Cl_2 release data of the CMA are shown in Fig. 3 together with that of CFCl_3 . If halocarbons with their main sources in the northern hemisphere have much shorter lifetimes, the ratios become much smaller than unity, and in cases of CHClCCl_2 and CCl_2CCl_2 , the ratios were almost zero with their very short lifetimes (a few months) (MAKIDE *et al.*, 1983).

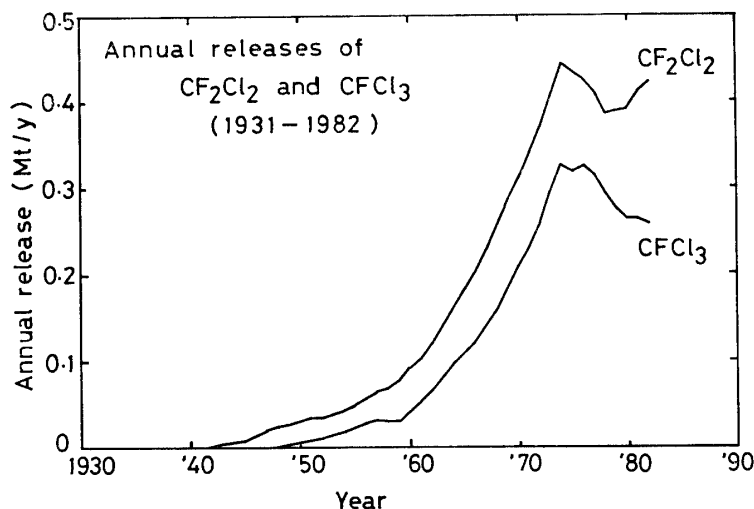


Fig. 3. Annual releases of CF_2Cl_2 and CFCl_3 (CMA, 1983). Annual releases have a maximum in 1974. After July 1971, their fractions in the southern hemisphere for the total annual releases were assumed to be 7.0% for CF_2Cl_2 and 5.5% for CFCl_3 . Prior to July 1971, their releases were assumed to be confined to the northern hemisphere (CUNNOLD et al., 1983a, b).

3.2. Vertical distribution

Air samplings on the "Pilatus PC-6" up to the altitude of 6.4 km were performed on January 24, 1983 around 69°S, 39°E. Vertical distributions of CF_2Cl_2 , CFCl_3 and N_2O are shown in Fig. 4. The temperature profile at 1500 LT is also shown in Fig. 4. Tropopause height was 8.6 km, and a small inversion was observed at 0.8 km.

Figure 4 shows that these gases were vertically well mixed. Mean values and standard deviations for five samples were 32_1 and $_3$ ppt for CF_2Cl_2 , 18_2 and $_8$ ppt for CFCl_3 , and 29_8 and $_2$ ppb for N_2O . Values of CFCl_3 seemed to decrease slightly with increasing altitude. That of CF_2Cl_2 , on the contrary, decreased at the lowest altitude (90 m). It cannot be ascertained from only one observation whether this was a true phenomenon or was due to the experimental uncertainties. In Fig. 4, differences of two measurements (larger than $_3$ ppt) for each sample are shown by error bars, while the average precisions of measurements at one atmosphere are shown in the last line of Table 2.

Mean volume mixing ratios of CF_2Cl_2 and CFCl_3 were lower than those observed over Japan from October 1982 to February 1983 by $(4 \pm 3)\%$ and $(6 \pm 7)\%$ respectively. As for CF_2Cl_2 , this value was smaller than that obtained from the latitudinal distribution (10%). Whether this discrepancy is only due to the experimental uncertainties or not will be examined elsewhere using further observations.

3.3. Time trend at Syowa Station

From February to December 1982, air samplings were performed once a month. Only one sample in February was carried back by JARE-22; the others were by JARE-23. Results are shown in Fig. 5, which includes values obtained by FUJI at 68.5°S and 38.7°E on January 1983, and rather large rates of increase of 2_8 ppt/year

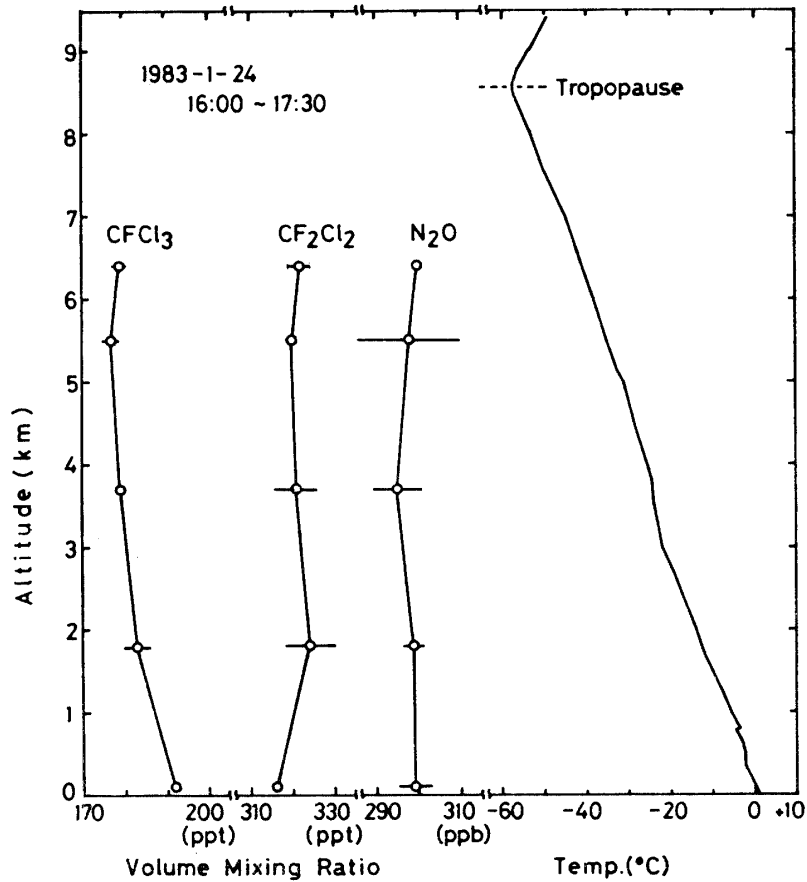


Fig. 4. Vertical distributions of CF_2Cl_2 , CFCl_3 and N_2O over Syowa Station. Temperature profile was obtained at 1500 LT.

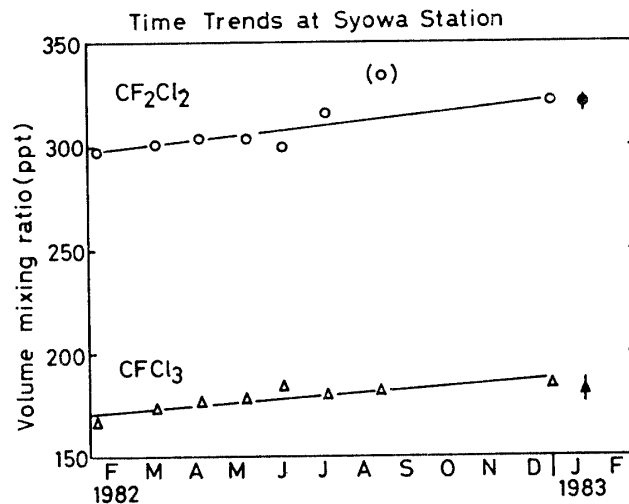


Fig. 5. Atmospheric volume mixing ratios of CF_2Cl_2 and CFCl_3 at Syowa Station during 1982.

○: CF_2Cl_2 , △: CFCl_3 , —: linear trend calculated by the method of least squares, ● and ▲: mean values obtained by the aircraft observation (Fig. 4). The sample on January 1, 1983 was obtained on FUJI at 68.5°S and 38.7°E .

for CF_2Cl_2 and 1_8 ppt/year for CFCl_3 were obtained by the method of least squares. The value of CF_2Cl_2 in August was too high and was excluded in the calculation. Solid marks (● and ▲) indicate mean values obtained by the aircraft observation which were not used in the calculation.

Samples from September to December showed very high values for CF_2Cl_2 and CFCl_3 . These samples would have been contaminated with the air on board in the return voyage, because these cylinders were packed in the upper side of the container and were not fixed firmly.

In Fig. 6, results of CFCl_3 are shown together with mean values obtained over Japan (HIROTA *et al.*, 1984). Results obtained in early 1982 by MAKIDE *et al.* (△ and ▲) (1983) were in good agreement with ours. R(N) and R(S) are results observed by RASMUSSEN *et al.* (1981) in the Pacific Northwest ($\sim 45^\circ\text{N}$) and at the South Pole. Multiplying by a calibration factor of 0.96 (RASMUSSEN and LOVELOCK, 1983), their values (R(N)) were also in good agreement with ours in 1979 and 1980. During 1982, the ratio of the mean volume mixing ratio at Syowa Station to that over Japan was about 0.93, which was nearly equal to the ratio of the mean value on January 24, 1983 to that over Japan in early 1983 (0.94), and which was larger than the ratio of 0.88 (R(S)/R(N)) in 1980 (RASMUSSEN *et al.*, 1981). MAKIDE *et al.* (1983) reported a rather small value (0.90) as the ratio in early 1982, which was also a little larger than 0.88. This can be interpreted by the long atmospheric lifetime of CFCl_3 (~ 80 years) (CUNNOLD *et al.*, 1983a) and by the pause in the increasing release since 1974 (Fig. 3).

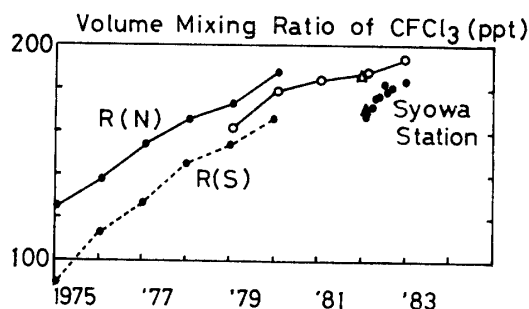


Fig. 6. Atmospheric volume mixing ratios of CFCl_3 .

●; Syowa Station, -○-; over Japan, ▲ and △; Syowa Station and Hokkaido (MAKIDE *et al.*, 1983), R(N) and R(S); Pacific Northwest ($\sim 45^\circ\text{N}$) and the South Pole (RASMUSSEN *et al.*, 1981).

The mean volume mixing ratio of N_2O from March to August and its standard deviation was 29_8 and $_3$ ppb. This mean value was equal to the mean value obtained on January 24, 1983 (Fig. 4). These results show that the N_2O mixing ratio in the Antarctic air was almost constant during 1982 within the range of experimental uncertainty.

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